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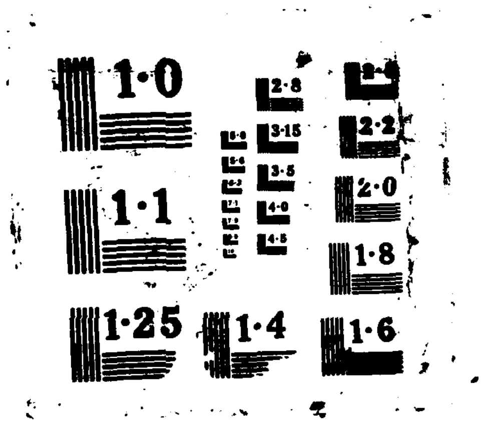
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In this study of the effects of rapid solidification on short-range order and magnetic properties, major progress and significant results were achieved in four specific areas. 1) Short-range order in $Co_{80}Nb_xB_{20-x}$ amorphous alloys was found to be similar at low x and dissimilar at large x to that of the equilibrium crystal structure. This key observation led to a broader model of magnetic properties in amorphous alloys. 2) Devitrification of two different metallic glasses led to technically and scientifically important discoveries related to the fine microstructures produced. 3) Theoretical cluster calculations of electronic structure significantly advanced our understanding of bonding and magnetism in amorphous alloys. Finally, 4), we found that magnetization reversal could be very well described by the soliton-like solutions to a realistic non-linear wave equation. This approach correctly describes the coupling of the wall motion to its own local strain field, a technically important effect.

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Effect of Rapid Solidification on Short-Range Order:
A Magnetic Study

Final Report

R.C. O'Handley

June 30, 1987

U.S. Army Research Office
Attn: Dr. A. Crowson

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I. INTRODUCTION

The research done under this contract is well described by the title of the program "Effects of Rapid Solidification on Short-Range Order: A Magnetic Study." Yet even under this general heading there is a diversity of topics and materials that were investigated. Part of this diversity is due to the fact that much of the first year of the program was spent completing important unfinished aspects of our earlier ARO contract (DAAG29-80-K-0088) on Metastable and Glassy Alloys. Also, the theoretical work on domain wall motion was begun under a STAS contract (DAAL03-86-M-0159) through Dr. A. Tauber at Fort Monmouth. This additional funding was sought because of an overlap of students whose support exceeded the budget limitations of the main contract. This exciting work was continued under the 84-K-0056 contract after expiration of the STAS.

The report organizes the research into four categories: 1) short-range order and magnetism in Co-B alloys with early transition metal substituents, 2) devitrification of amorphous alloys to produce novel microstructres and new magnetic effects, 3) cluster calculations of electronic structure of amorphous alloys to explain their stability and magnetic properties, and 4) magnetization reversal in amorphous alloys under pulse power conditions. Papers published under this contract are listed as references 1 to 11. Other references cited in the report begin with number 12.

II. RESULTS AND DISCUSSION

1) Magnetism and Short-Range order in Co-base glasses

Because of their low magnetostriction, cobalt base glasses are less stress sensitive and show superior soft magnetic properties, especially at high-frequency, compared to iron-base glasses. We have aggressively pursued important leads that link their low magnetostriction to their short-range order (SRO).[12]

Considerable evidence suggests that certain cobalt base glasses can undergo a reversible transformation from one amorphous SRO to another.[13] This transformation has important effects on magnetostriction, causing its temperature dependence to depart sharply from that predicted theoretically.[1] The temperature of the anomaly in amorphous alloys shifts with sample composition in a manner consistent with the shift in transformation temperature of comparable crystalline alloys.

To get a clearer understanding of the SRO in these materials, extensive magnetic and x-ray scattering studies were done on a series of Co-Nb-B glassy and crystalline alloys.[2] The most important result is observed in the series $Co_{80}Nb_xB_{20-x}$. For $x < 8$ at%, the *saturation moments* of the glassy and crystalline alloys are similar suggesting similar SRO. In that region the crystalline phases are generally close packed (fcc) and the cobalt atoms are highly coordinated by cobalt. For $x > 10$ the saturation moments of the glassy alloys are greater than those of the crystalline phases, suggesting dissimilar SRO. In this region the equilibrium crystal structure is the Laves phase Co_3Nb with only 6 cobalt neighbors around each cobalt. The more random site occupation in the glassy structure results in *greater cobalt-magnetic moments*. These observations have led to the development of a more general model for magnetic moments in disordered alloys that is also able to explain moment anomalies in rare-earth containing alloys and in quasicrystals.[3]

These studies are being extended to the Co-Mo-B and Co-Zr-B systems with a particular aim of understanding the different magnetic moment suppression caused by

Mo and Zr in the presence of B.[4]

2) Devitrification of Amorphous Alloys

Controlled devitrification of amorphous alloys can result in superfine microstructures, sometimes with metastable phases, that can give rise to unusual magnetic behavior.

An extensive study of devitrification of $Co_{84}Nb_{10}B_6$ showed two important effects.[5] First the coercivity increased through the early stages of devitrification, peaked and then decreased slowly through complete crystallization in a way predicted by theory for interaction of domain walls with fine precipitates.[14] This is the first verification of the theory in a single sample heat treated to produce particles of increasing size. The final crystallized ribbons showed semi-hard magnetic properties (H_c in excess of 100 Oe) yet remained extremely ductile because of their unique microstructure. A patent application has been filed on this effect (Serial No. 729,278).

Similar studies in an iron base glass $Fe_{43}Cr_{25}Ni_{20}B_{12}$ have given different but equally important and interesting results.[6] Because of the high Cr and Ni content, the Curie temperature of this glass is well below room temperature. In the early stages of devitrification, a fine dispersion of α-Fe particles is observed to precipitate from the amorphous matrix. These particles cause the material to become ferromagnetic at room temperature. Upon further annealing, the material loses its ferromagnetism due to partitioning of the solutes in the amorphous and crystalline parts of the sample. The fine dispersion of magnetic particles produced in the early stage of devitrification lends itself to characterization by its superparamagnetic behavior. Analysis of such behavior shows the particles to have net moments in the range 3 to 6 x 10^4 μ_B and diameters on the order of 100 to 140 Å. These values are consistent with an assumed moment of $1\mu_B$ per transition metal atom and with TEM observations, respectively.

3) Electronic structure, Stability and Magnetism of Amorphous Alloys

Interaction with Prof. Keith Johnson by making use of his molecular orbital methods of determining electronic structure and physical properties of metastable phases has been an important aspect of our work since the original program in which he was formally involved (DAAG29-80-K-0088). Because the atomic positions in a finite cluster need not satisfy classical crystallographic constraints or periodic boundary conditions, these calculations are well suited for modelling the behavior of noncrystalline materials. Moreover, the molecular orbital topology at the Fermi level has been found to be important to glass stability[15] and to structural transformations including melting and the glass transition.[7] Glass transition temperature and melting temperature were calculated quite accurately for nine metals.

More recently we have extended these calculations to tetrahedral iron clusters which may contain a metalloid atom (B,C,N,Si) at the center.[8] The results reveal that two types of bonding interactions are important in metal/metalloid (T/M) glasses, a more polar T(spd) - M(s) bonding and a predominantly covalent T(d) - M(p) bonding. The former is mainly responsible for the stability of the alloy and the latter is shown to have a strong influence on magnetic properties because of the delocalization of the 4d orbitals it involves. Even in these small clusters we were able to calculate reasonable magnetic moments: $Fe_4(3\mu_B/Fe)$, $Fe_4B(2.6\mu_B/Fe)$, Fe_4Si $(2.4\mu_B/Fe)$, $Fe_4C(0.2\mu_B/Fe)$, and $Fe_4N(0.0\mu_B/Fe)$. The variation reflects the increasing covalent bonding and decreasing state density at E_F from B to N.

4) Magnetization Reversal in Amorphous Alloys

Amorphous alloys show promise for pulse-power applications because of their relatively high electrical resistivity, their low magnetic anisotropy and their homogeneity. Yet their losses under pulse-power conditions are still not well described by classical saturation wave theory. Furthermore, the possibility exists that under favorable conditions the magnetization reversal front could penetrate beyond the classical skin depth if it were coupled to a magneto-elastic wave. In order to explore these effects theoretically we have used soliton-like solutions to the non-linear wave equations describing domain wall motion under more realistic conditions than has been done heretofore.[9,10] Our results for domain wall velocity reduce correctly to Kittel's linear dependence on field in the weak field limit and correspond to Walker's exact solution in the limit of vanishing anisotropy. However, our solution is not ill behaved like the Walker solution at high anisotropy.

Finally, solution for the local strain around the domain wall indicates that it is possible to draw a domain wall along by coupling it to an elastic shear wave.

III. SUMMARY

Many of these results have been incorporated in a major review paper which I was invited to prepare by the editors of Journal of Applied Physics.[11]

The results obtained through this ARO program have added significantly to our fundamental understanding of magnetism, bonding and short-range order in amorphous alloys. They have also pointed to new technological opportunities in devitrified glasses and in application of amorphous ribbons to pulse-power applications.

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(Refernces 1 - 11 were published directly as a result of this ARO contract. References 12 - 15 are also cited in the Final Report text).

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Students Supported under this Contract

Undergraduates

Y.K. Oh	S.B.	1986
T.C. Lau	S.B.	1986
V. Kwapong	S.B.	1987
Karen Dickson	S.B.	1987
D. Dismukes	S.B.	1988

Graduate Students

Y. Hara	Ph.D.	Sept. 1986
H. How	Ph.D.	Sept. 1987

INVENTIONS

"Ductile Permanant Magnets Formed by Devitrification of Co-Nb-B Glass," U.S. Patent application Serial No. 729,278, J. Megusar, R.C. O'Handley and N.J. Grant.

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